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Procedia Materials Science 1 (2012) 403 – 409

Procedia Materials Science

www.elsevier.com/locate/procedia

11th International Congress on Metallurgy & Materials SAM/CONAMET 2011.

Zirconia reinforcement of cement free Alumina refractory castables by two routes

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Abstract

The cement free castables (CFC) and the ultra low cement castables (ULCC) differ from the conventional castables not only in the fact that alumina cement content and that the water required for elaboration is considerable lower, but also that they exhibit outstanding physical-chemical properties and mechanical properties. In this work we compared two routes of introducing zirconia to cement free alumina castables with a zirconia free castables, one by adding electrofused zirconia grains and the second by incorporating reused grains from electrofused AZS block formerly used as floor of glass melting furnaces. Comparable microstructures and textural properties were achieved, this fact permitted to evaluate the zirconia influence in the mechanical and fracture properties of the studied materials. There was a direct correlation with the zirconia content of both the mechanical properties at room temperature and at high temperatures (1350°C). Finally, while at room temperature the incorporation of AZS grains proved to be more efficient to reinforce electrofused zirconia proved to be the most effective additive for reinforcement of castables studied if they were to be used at elevated temperatures.

Key words: Zirconia, Refractories, Castables

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2211-8128 © 2012 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of SAM/CONAMET 2011, Rosario, Argentina. Open access under CC BY-NC-ND license. doi:10.1016/j.mspro.2012.06.054

1. Introduction

The cement free castables (CFC) and the ultra low cement castables (ULCC) differ from the conventional castables not only in the alumina cement content. Due to the formation of liquid phases at high temperature but also the water required for elaboration is considerable lower in comparison this gives them outstanding physical-chemical properties and mechanical properties, Lee et al. 2001.

Significant toughening can be obtained by incorporating zirconia particles (ZrO2) in a ceramic matrix. Different mechanisms are involved in the toughening: stress-induced transformation, microcraking, crack bowing and crack deflection. In all cases, the operative toughening mechanism depends on such variables as matrix stiffness, zirconia particle size, chemical composition, temperature and strength, Qi-Ming et al. 1986, Rendtorff and Aglietti 2010, Rendtorff et al. 2010.

Since there are several ways of incorporating zirconia, the main objective of this study is to compare two ways of introduction of such a phase: one by adding electrofused zirconia grains and the second by incorporating reused grains from electrofused AZS block formerly used as floor of glass melting furnaces Duvierre et al.1999, Duvierre et al.1995, Evans 2005. In order to evaluate the effects of the introduction of zirconia a zirconia free castables was also developed.

In particular, the objective of this study is to determine the influence of the introduction of monoclinic zirconia (m-ZrO_2) on the textural properties, microstructure, mechanical and thermomechanical properties of cement free castables with technological interest.

2. Experimental procedure

A homogeneous dry mixtures of all the starting powders was carried out, the required amount of water was incorporated together with a poliacrilate based dispersant. Prismatic samples were vibrocasted (25x25x150 mm3). Afterwards the samples were dried in air for at least 24 hours and later dried in stove (110ºC) up to constant weight. Samples were sintered in an electric kiln at 1400ºC with 2 hours soaking. Both the heating and cooling rates employed were 5ºC/min. The actual castables formula is shown in table 1.

Table 1. Studied castables composition

Material	HA	HAZS	HZ
Tabular Alumina (diverse mesh between mesh 6 and mesh 325)	85%	70%	70%
Calcined Alumina	10%	10%	10%
Microsilica	4,5%	4,5%	4,5%
Alumina cement Secar 71	0,5%	0,5%	0,5%
AZS (<mesh 30)	---	15%	---
Electrofused ZrO_2 (between mesh 200 and mesh 325)	---	---	15%

Density and open porosity of sintered samples were determined by the water absorption method. Crystalline phases formed were analyzed by X-ray diffraction (XRD) (Philips 3020 equipment with Cu-Ka radiation in Ni filter at 40 kV– 20 mA).

The Microstructural examination was conducted with a scanning electron microscope SEM (Quanta 200 MK2 Series de FEI). The examination was carried out after polishing the surface with 0.25 mm diamond paste.

The dynamic elastic modulus E of the composites was measured by the excitation technique with a GrindoSonic, MK5 ''Industrial'' Model, described in: Radovic et al. 2004.

Flexural strength (σ_f) was measured on the bars with rectangular section using the 3-point bending test with 125 mm of span and a displacement rate of 1 mm/min was employed (universal testing machine INSTRON 4483).

The fracture toughness (K_{IC}) and the fracture initiation energy (γ_{NBT}) were evaluated by the single edge notched beam method, Kubler 1997, using notched bars with notches of 0.3mm wide and depths between 0.5 and 10mm. in the same universal testing machine but with a 0.1 mm/min rate. In this method K_{IC} is given by:

$$K_{IC} = \frac{3QLC^{1/2}}{2WD^2}\left[A_0 + A_1\left(\frac{C}{D}\right) + A_2\left(\frac{C}{D}\right)^2 + A_3\left(\frac{C}{D}\right)^3 + A_4\left(\frac{C}{D}\right)^4\right] \qquad (1)$$

where Q is the load applied to the notched bar in kg, L is the span, C is the depth of the notch, D is the thickness of the specimen, is the width of the specimen, and A0, A1, A2, A3 and A4 are functions of the ratio (L/D) described in , Kubler 1997; Rendtorff and Aglietti 2010. In the same method; Rendtorff and Aglietti 2010 where γ_{NBT} can be expressed as

$$\gamma_{NBT} = \frac{{K_{IC}}^2}{2E} \qquad (2)$$

Finally the critical crack length (L_c) can be estimated from Eq. (3) Rendtorff and Aglietti 2010.

$$L_c = \left(\frac{K_{IC}}{\sigma_f\sqrt{\pi}}\right)^2 \qquad (3)$$

3. Results and discussions

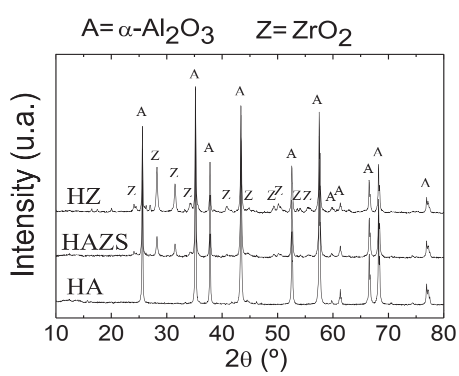

Fig 1: Diffraction patterns of the cement free alumina castables (A: α-Al_2O_3, Z: ZrO2)

Fig. 1 shows the diffraction patterns of the three castables alter sintering at 1400ºC. As expected, in HA the only phase detected is the alumina, but in HAZS and HZ the alumina peaks are accompanied by monoclinic zirconia. Logically HZ presents a higher zirconia content (HA < HAZS < HZ).

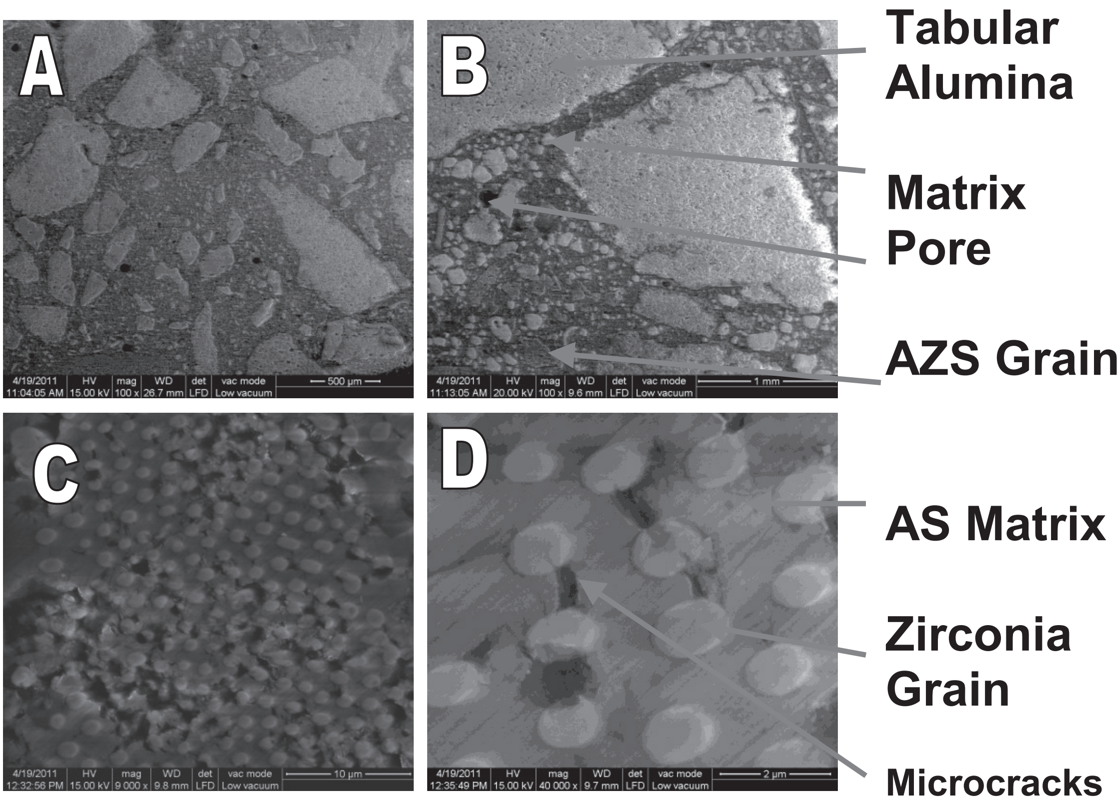

Fig 2: SEM images of the alumina castables. A) Typical microstructure of the three studied castables (HA, HAZS, HZ), B) HAZS microstructure, C) y D) microstructure of the AZS grains.

Figure 2 shows SEM images of the polished (diamond paste 1μm) samples. Figure 2A shows the typical distribution of coarse electrofused alumina grains (light grey) imbibed in fine grained matrix (dark grey). The tree studied materials presented this microstructure. Figure 2B shows the microstructure that corresponds to the HAZS material. Together with the described arrays, some close pores can be detected in black. Particularly some AZS grains can be observed as well in HAZS castables. On the other hand the zirconia grains could not be detected in the fine matrix. The typical AZS grains microstructure do not changes during the castables processing. This microstructure consists in rounded micron size monoclinic zirconia imbibed in an electrofused alumina matrix sintered with an important amount of glassy phase Duvierre et al.1999, Duvierre et al.1995, Evans 2005. The AZS microstructure is shown in figures 2C and 2D. Finally, the also typical microcracks of the AZS microstructure were observed. These microcracks can absorb both mechanical and thermals stress Evans and Faber 1984, Ruehle et al. 1986, Ruehle et al. 1987. With already measured reinforcement of these kinds of multicomponent ceramics, Rendtorff and Aglietti 2010, and Rendtorff et al. 2010.

Table 2 shows the textural properties castables. The contraction after heat treatment (1400°C) was low enough and similarly the three castables. The obtained values of densities and porosities correspond to dense alumina cement free castables, Lee et al. 2001. Also is important to point out that as the achieved values are similar, the results of the macroscopic properties, like mechanical properties, of these materials can be compared.

Table 2. Textural properties of the cement free castables.

Properties	HA	HAZS	HZ
Density (g/cm3)	3.64	3.6	3.79
Porosity (%)	13.9	12.2	13.3
Contraction (%)	-0.47	-0.72	-0.32

Zirconia undergoes martensitic transformation from monoclinic to tetragonal phase at around 1100ºC in a heating (semicycle) step and the inverse transformation during cooling occurs around 900ºC, but it has been stated that if the grain is smaller than a critical size the tetragonal phase is retained Rendtorff et al. 2011A and Rendtorff et al. 2011B.

This transformation is accompanied by a volume change and together with the thermal expansion mismatch of alumina and zirconia (5.10-6 °C-1 and 10.10-6 °C-1) are the mechanisms responsible for the formation of microcracks in the microstructure that deteriorates mechanical properties of these materials. However, Rendtorff et al.2011A, Rendtorff et al.2011B, the resulting strength is enough for the service (or installation) of these castables, Lee et al. 2001. On the other hand, the mechanical strength at elevated temperature (similar to the service) was considerably improved by the introduction of zirconia. While the addition AZS of doubled the Hot-MOR, the addition of zirconia electrofused tripled the strength of these materials at elevated temperatures. The actual values of the mechanical properties of the studied castables are shown in Table 3.

It is observed that at room temperature both the mechanical strength (MOR) and the dynamic modulus of elasticity (E) decrease with the addition of zirconia by the chosen two routes. In other words, the addition of m-ZrO_2 by the two studied routes decreases the mechanical properties at room temperature. This could be explained by the development of microcracks in the matrix due to the presence of zirconia. Furthermore, while in the HAZS microcracks exist within AZS grains, which act as a cut over tabular alumina and deterioration in the HZ occurs throughout the processing at high temperatures in the fine grains matrix. In HZ the electrofused zirconia is a constituent of the matrix.

Table 3. Textural properties of the cement free castables.

Properties	HA	HAZS	HZ
MOR (MPa)	66	44	33
Hot MOR (MPa)	1,4	3,4	5,5
E (GPa)	123	115	69
K_{IC} (MPa.m1/2)	2,47±0.2	2,68±0.25	1,79±0.3
γ_{NBT} (J/m^2)	37	41	11
L_c (mm)	0,45	1,18	0,94

The effect of the incorporation of zirconia is different in the fracture properties at room temperature (K_{IC} and γ_{NBT}). While the properties AZS improves slightly the fracture properties (but within the error of the technique); the incorporation of zirconia electrofused deteriorates the fracture toughness of castables. Finally, the critical length of the zirconia containing castables was increased showing an important change in the microcracks and defects distributions in the castables this fact improves the castables properties and behaviours, Lee et al. 2001, and Rendtorff and Aglietti 2010.

4. Conclusions

We compared two routes of introducing zirconia to cement free alumina castables with a zirconia free castables, comparable microstructures and textural properties were achieved, this fact permitted to evaluate the zirconia influence in the mechanical and fracture properties of the studied materials.

There was a direct correlation with the zirconia content of both the mechanical properties at room temperature and at high temperatures (1350°C). While the incorporation of zirconia results in a decrease (controllable) at room temperature mechanical properties (MOR and E), at high temperatures the addition of zirconia in the matrix tripled the strength of these materials. However, while at room temperature the incorporation of AZS grains proved to be more efficient to reinforce electrofused zirconia proved to be the most effective additive for reinforcement of castables studied if they were to be used at elevated temperatures. The critical length of the zirconia containing castables was increased showing an important change in the microcracks and defects distributions in the castables this fact improves the castables properties and behaviours.

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